Application of the Diels−Alder Reaction to Polymers Bearing Furan Moieties. 2. Diels−Alder and Retro-Diels−Alder Reactions Involving Furan Rings in Some Styrene Copolymers

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ABSTRACT: Styrene copolymers containing various amounts of a novel comonomer bearing a pendant furan ring were synthesized and characterized before being submitted to Diels−Alder reactions with either a monomaleimide or a bismaleimide. Spectroscopic evidence, supported by data from model compounds, indicated that the resulting linear and cross-linked products contained extensive percentages of adduct structures formed from the furan moieties. Both types of materials were then heated in a solvent containing a large excess of 2-methylfuran in order to induce the retro-Diels−Alder and the coupling of the released maleimides with the furanic additive. The reaction proceeded as expected and the original copolymers could be recovered from the treatment. The interest in the general strategy reported here resides in the possibility of recycling cross-linked polymers by a simple thermal treatment conducted in the presence of a suitable trap.

Introduction

The Diels−Alder (DA) reaction generally involves the coupling of a "diene" with a "dienophile". A vast array of intra- and intermolecular DA reactions have been studied for both mechanistic and synthetic reasons.[1,2] One of the many interesting features of the DA reaction is the readiness of many adducts to undergo the reverse reaction when heated to an appropriate temperature, thus regenerating the original reactants.[3] The application of DA chemistry to polymer synthesis,[4−8] modification,[9−11] and (reversible) cross-linking[9,12−18] has received some attention, but much remains to be done to exploit the potential of the DA reaction to provide access to novel materials.

The furan ring is one of the most thoroughly studied dienes in DA reactions, although not all furans are apt to undergo this type of cycloaddition.[1,2] Various strategies can be envisaged to synthesize or modify polymer structures by exploiting the reactivity of this heterocycle with various dienophiles. This topic was reviewed very recently,[19] so only a brief survey of the most pertinent literature will therefore be given here. Three distinct strategies have been explored, namely (i) the stepwise polymerization through complementary functions, e.g., bisfurans plus bisdienophiles;[4−8,20] (ii) the chemical modification of polymers bearing moieties which are prone to the DA reaction, e.g., the coupling of pendant furan moieties with a monodienophile[9−11] or the cross-linking of the same type of polymer with a bisdienophile;[9,12−15,18] (iii) the ring-opening metathesis polymerization (ROMP) of DA adducts.[21−24]

Owing to the limited amount of published work on these topics and the long-standing interest of one of our laboratories in the study of furan-based polymers,[19,25−27] a more systematic exploration of their reactions has been undertaken, with particular emphasis on strategies (i) and (ii). In the previous paper of this series,[9] polyurethanes and acrylic copolymers bearing furan heterocycles in the main chain or as side groups were reacted with mono (e.g., N-substituted maleimides) and bisdienophiles (e.g., bismaleimides) in order to assess their readiness to undergo the DA reaction as a function of the steric availability of the furan ring.

The present study concerns the synthesis of styrene copolymers bearing pendant furan moieties and their DA-based modifications with mono or bisdienophiles, including the application of the retro-Diels−Alder (RDA) reaction. Schemes 1 and 2 summarize our synthetic approach to the various phases of this work, viz., (i) the two ways of preparing random copolymers; (ii) the DA reaction between the pendant furan moieties and mono and bisdienophiles, and (iii) the RDA procedures applied to these polyadducts. The details of these procedures and the results obtained are discussed below.

Experimental Section

Monomers. Commercial styrene (**1**) was washed with 10% aqueous NaOH, dried over magnesium sulfate, and then fractionally distilled under reduced pressure. Commercial 4-chloromethylstyrene (**2**) was fractionally distilled under vacuum. 4-Furfuryloxymethylstyrene (**3**) was synthesized by the O-etherification of **2** with furfuryl alcohol using phase-transfer catalysis, as follows: the alcohol was stirred with 33% aqueous NaOH for 1 h before the addition of a toluene solution of **2** ([OH]/[Cl] = 2) and a 40% aqueous solution of tetrabutyl ammonium hydroxide (10% mol/[OH]) as the catalyst. The mixture was stirred for 48 h at room temperature before the addition of an excess of water. The organic products were recovered by multiple extractions with diethyl ether. The combined extracts were treated several times with water to remove the unreacted furfuryl alcohol and dried over magnesium sulfate and the solvents evaporated. The residue (76% yield with respect to **2**) was characterized by FTIR and ^{1}H- and ^{13}C-NMR spectroscopy.

Homo- and Copolymerizations and O-Etherification of the Chloromethyl Moieties. The free radical homopolymerizations of **2** and its copolymerizations with **1** (using

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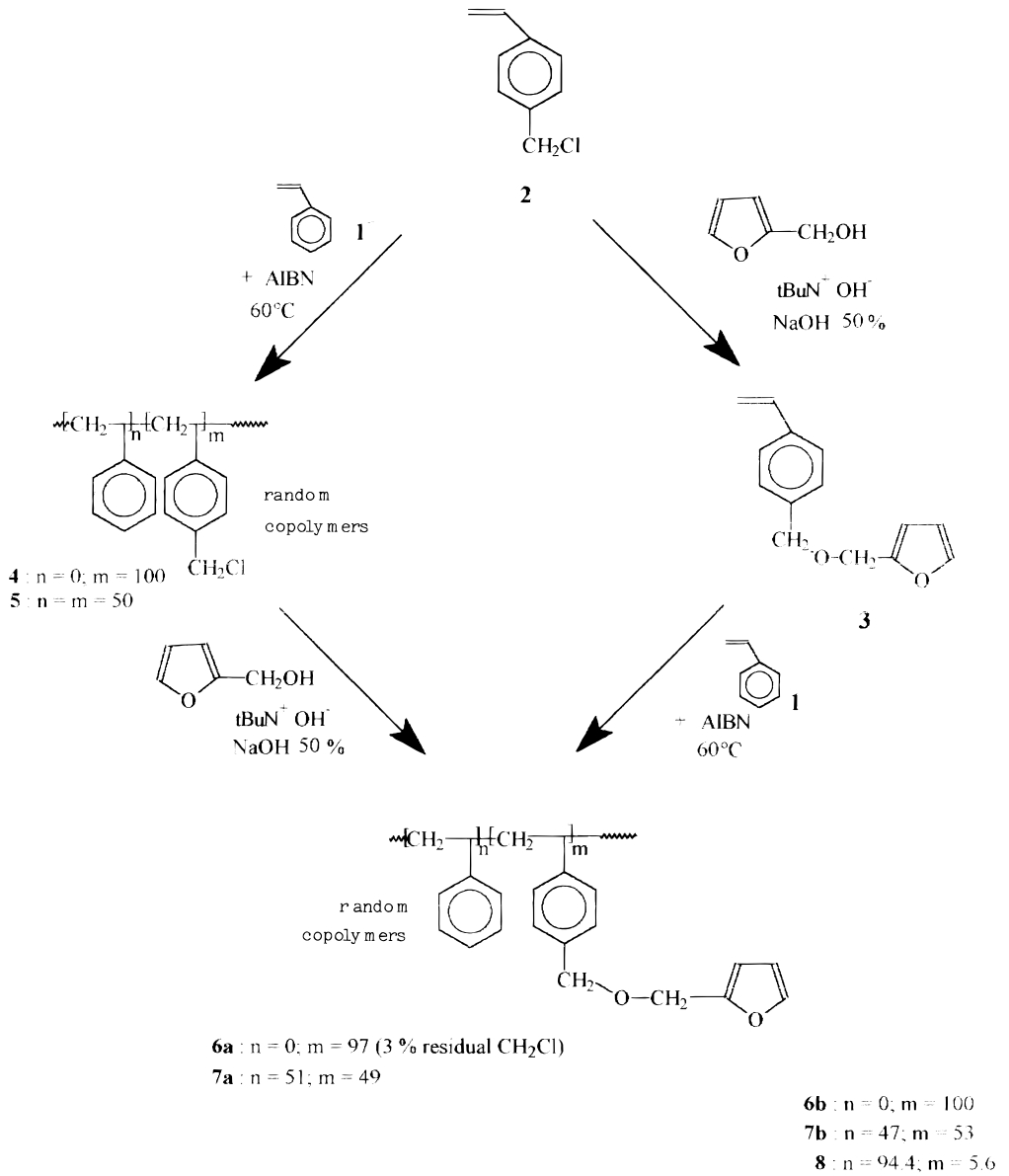
Scheme 1



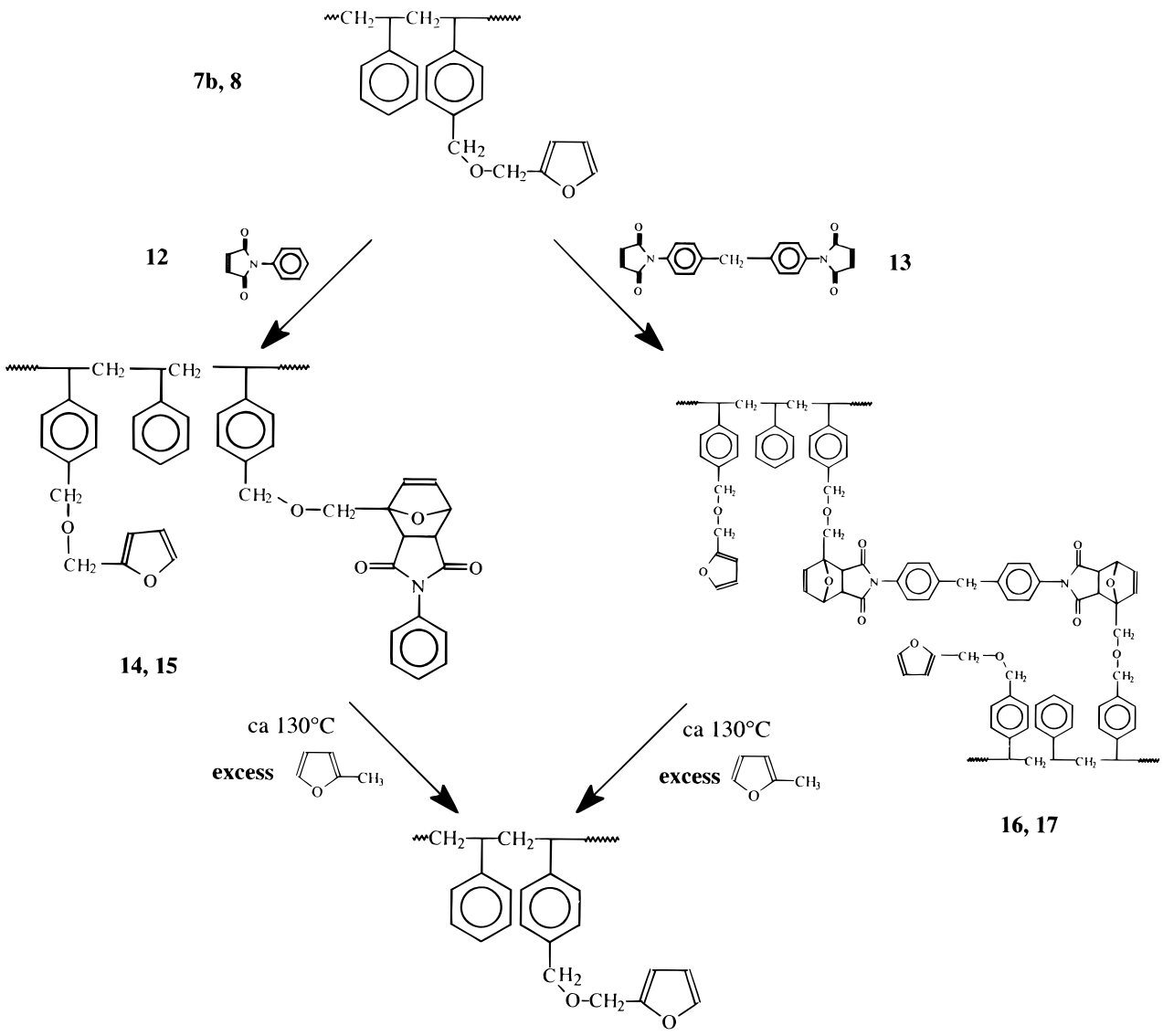
equimolar amounts) were conducted in a glass tube equipped with a rotaflo stopcock. The monomers were dissolved in an equal volume of toluene and 1% w/w of AIBN was added. After a thorough degassing of the resulting solutions, the mixtures were heated at 60 °C and left under vacuum for 24 h. The resulting polymers (**4** for the homopolymer of **2** and **5** for the 50/50 copolymer of **1** + **2**) were precipitated into an excess of methanol, isolated, and vacuum dried to constant weight. Yields varied between 60 and 70%. Each product was characterized by FTIR and ^{1}H-NMR spectroscopy and by GPC (THF solutions passed through a standard series of styragel columns, calibrated with monodisperse polystyrene samples, with refractometric detection).

Polymers **4** and **5** ($M_n \cong 30\,000$, $M_w \cong 50\,000$) were modified by the O-etherification procedure already described above for the conversion of monomer **2** into monomer **3,** except that (i) a 5/1 molar excess of furfuryl alcohol was used with respect to the chloromethyl groups present and (ii) the modified material was isolated by precipitation into methanol and vacuum drying. The resulting polymers, **6a** and **7a**, respectively, were characterized by FTIR and ^{1}H-NMR spectroscopy (which confirmed the expected structures) and by GPC: M_n increased by about 10% and M_w by ca. 20%. The yields of O-etherification ranged between 93 and 99%.

Monomer **3** was both homopolymerized and copolymerized with **1** (50/50 and 5/95 initial molar monomer feed) according to the free-radical procedure described above. The ensuing products, isolated in 70−80% yields, respectively **6b**, **7b**, and **8**, were characterized by FTIR and ^{1}H-NMR spectroscopy, DSC, GPC, and elemental analysis after a double precipitation into an excess of methanol and drying to constant weight.

Model Adducts. In order to facilitate the correct structural assessment of the DA adducts of the furan-containing polymers and to be able to verify the occurrence of the RDA reactions, two model compounds were synthesized, namely, the adducts **9** and **10** resulting respectively from the DA reaction of 2-methyl furan (**11**) with *N*-phenylmaleimide (**12**) and *N*,*N*′-bismaleimido-4,4′-diphenylmethane (**13**). The three reagents were commercial samples from Aldrich, with purities ranging from 97 to 99%. The diene and the dienophile were dissolved in dichloromethane by using equimolar amounts for **9** and a fourfold molar excess of the furan derivative for **10**. The solutions were heated under reflux for 24 h and the ensuing products precipitated into diethyl ether, filtered off, and dried. With this procedure, only the exo-adducts were obtained,. Mixtures of exo- and endo-isomers were obtained when the DA syntheses were carried out in bulk. The structure of **9** (mp 117 °C for the endo- and 130 °C for the exo-isomer) and **10** and their stereochemistry were established by FTIR and

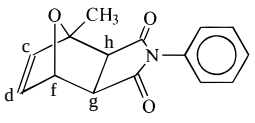
Scheme 2



^{1}H-NMR spectroscopy. With the latter we obtained the following data (ppm from TMS in $CDCl_3$) for **9**: CH_3 1.8 (exo) and 1.9 (endo), g 2.9 (exo) and 3.25 (endo), h 3.15 (exo) and 3.80 (endo), f 5.30 (exo) and 5.32 (endo), d 6.35 (exo and endo), c 6.55 (exo and endo), and aromatic protons between 7.2 and 7.45 for both isomers; for **10** the resonances occurred essentially at the same chemical shifts and the central CH_2 resonated at 4.0 ppm. The elemental analysis of **9** gave C 69.76% (calcd 70.59), H 4.95% (calcd 5.10), N 5.38% (calcd 5.49) and O 18.40% (calcd 18.82), whereas that of **10** suggested some oxidation, viz., C 69.80% (calcd 71.27), H 5.40% (calcd 4.98), N 5.32% (calcd 5.36), and O 19.84% (calcd 18.39).

DA Reactions Involving Polymers. The formation of polyadducts from the DA reaction of the pendant furan rings in **7b** and **8** with the monodienophile **12** was conducted as follows: the polymer and a fourfold molar excess of **12** were dissolved in dichloromethane and heated under reflux in a nitrogen atmosphere for 24 h. The resulting products **14** (**7b** + **12**) and **15** (**8** + **12**) were precipitated into methanol, redissolved in methylene chloride, reprecipitated in methanol, collected, and vacuum dried before being characterized by FTIR and ^{1}H-NMR spectroscopy, GPC, and elemental analysis.

The corresponding reactions of the same copolymers with bisdienophile **13** were carried out by the same procedure, except that the furan/dienophile initial ratio was 1:1. The resulting gels **16** (**7b** + **13**) and **17** (**8** + **13**) were isolated by centrifugation, washed several times with methylene chloride, vacuum dried, and characterized by FTIR spectroscopy and elemental analysis.



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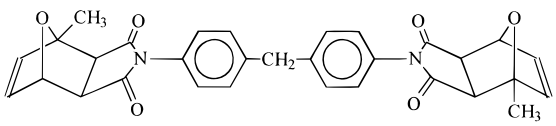

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RDA on Polyadducts and Gels. All RDA reactions were carried out in the presence of a very large excess of **11** in order to trap the dienophile released. Typically, 0.2 g of polyadducts **14** and **15** as well as gels **16** and **17** were placed in 20 mL of a chlorobenzene/2-methylfuran 80/20 v/v mixture and heated at 130 °C for various reaction times, viz., 24 h for **15** and **17** and, on account of their higher adduct content, 48 h for **14** and **16**. The resulting products were precipitated into methanol and collected by filtration. The filtrate was saved in order to identify the adducts with **11** and the dried precipitates were

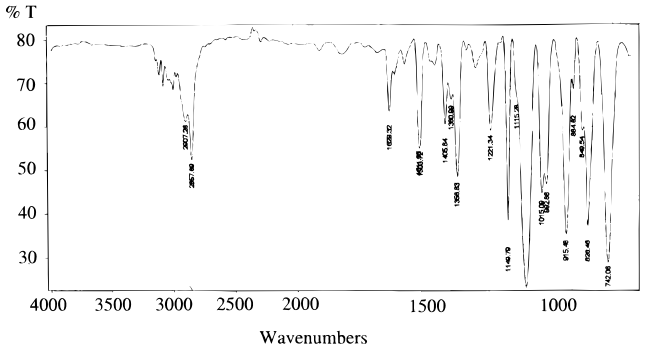

Figure 1. FTIR spectrum of **3**.

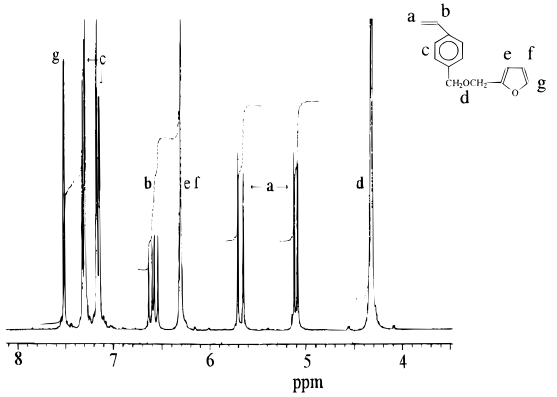

Figure 2. ^{1}H-NMR spectrum of **3** in DMSO-d_6.

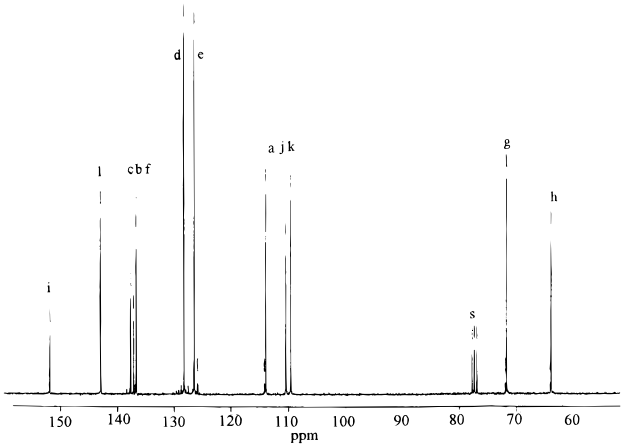

Figure 3. ^{13}C-NMR spectrum of **3** in $CDCl_3$.

characterized by FTIR and ^{1}H-NMR spectroscopy and elemental analysis.

Results and Discussion

Structure of Monomer 3. To the best of our knowledge, compound **3** has not been reported previously. Figure 1 shows the FTIR spectrum of **3** in which the most relevant peaks, other than the typical absorptions of the C2 monosubstituted furan ring and the 1,4-disubstituted benzene ring, were those arising from the ether linkage at 1075 and 1149 cm^{-1} and from the vinyl group at 1629 cm^{-1}. Figures 2 and 3 give the ^{1}H- and ^{13}C-NMR spectra of this new monomer with the corresponding assignments. The expected structure was thus clearly verified by this spectroscopic analysis which indicated moreover the absence of any detectable impurity, particularly of the two reagents used to prepare **3**. This was confirmed by gas chromatography.

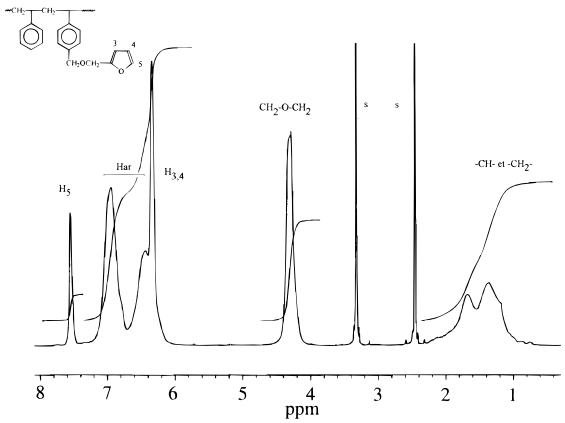

Figure 4. ^{1}H-NMR spectrum of **7a** in DMSO-d_6 (the corresponding spectrum of **7b** was identical).

Table 1. Amount of Pendant Furan Rings Present on Polymers and Copolymers, as Determined by ^{1}H-NMR Spectroscopy and Elemental Analysis of the Copolymers

polymer (see Scheme 1)	elemental analysis, %	% of furanic units
7b	C82.85, H 6.36, O 10.20	53
6a		97 (3% CH_2Cl)
7a	C 82.90, H 6.54, O 10.12	49
8	C 90.96, H 7.60, O 1.33	5.6
6b		100

Polymerizations and O-Etherification of Polymers. Two different routes were used to synthesize the styrene copolymers **7** and **8** which contained various proportions of pendant furan rings, viz. (see also Scheme 1), (i) copolymerizations of **1** with **2** followed by O-etherification with furfuryl alcohol, which was used to prepare **7a**, or (ii) copolymerizations of **1** with **3,** which was used to prepare **7b** and **8**.

The homopolymer **6a** was synthesized in order to facilitate the study of the O-etherification and the DA and RDA reactions. We wished initially to determine the extent of substitution in the O-etherification and the absence of hydrolysis of the chloromethyl groups to give CH_2OH. The FTIR and ^{1}H NMR spectra confirmed the latter point, and, based on the integration of the residual peak at 4.5 ppm arising from the CH_2Cl protons, indicated that in fact only about 3% of chlorinated moieties had not been replaced by furan rings. The lack of completion of the O-etherification could be attributed to steric effets related to incomplete accessibility to the reactive sites on the starting polymer **4**.

The FTIR and ^{1}H NMR spectra of **7a** and **7b** were practically identical, thus corroborating the equivalence of the two alternative methods of synthesis. Figure 4 shows a typical ^{1}H NMR spectrum of copolymer **7a** with the corresponding assignments for the proton resonances. The FTIR spectrum gave the expected peaks corresponding to both comonomer units and no absorption around 1630 cm^{-1} indicating the disappearance of the vinyl moieties. The spectroscopic features of furan-poor copolymer **8** were qualitatively similar to those encountered with **7** but showed of course correspondingly weaker signals for the heterocycle.

Table 1 summarizes the compositions of these various polymers as determined by ^{1}H-NMR spectroscopy and elemental analysis. The excellent agreement between **7a** and **7b** confirmed the high efficiency of both ways of preparing the copolymers. Also, the contents of furan rings obtained from the spectra of the copolymers were

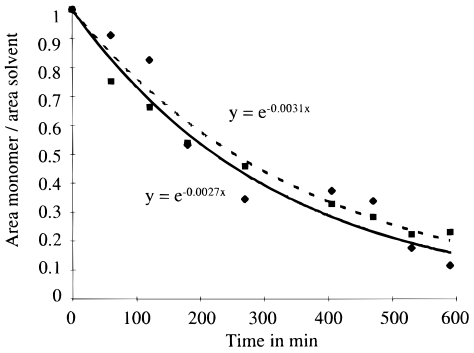

Figure 5. Relative rate of comonomer consumption of ◆ styrene (**1**); ■ furanic monomer (**3**); — best exponential fit for **1**; - - - best exponential fit for **3**.

very close to those calculated from their elemental analysis. The molecular weights of these materials, averaged over three syntheses for each copolymer, were $M_n = 30\,000$ and $M_w = 58\,000$ for **8** and $M_n = 44\,000$ and $M_w = 150\,000$ for the **7b**. Those of homopolymer **6b** were $M_n = 20\,000$ and $M_w = 70\,000$. The relatively high value M_w/M_n for **7b** and **6b** suggests that some grafting might have occurred as a result of side reactions induced by the presence of high concentrations of furan moieties, as already reported in the free radical polymerization of certain furan monomers.[19,25]

The kinetics of the copolymerization of **1** with **3** were followed by monitoring the decrease in the concentration of each monomer by GLC. Figure 5 shows the specific instance of a 50/50 run in which the rate of monomer consumption was essentially the same for the two comonomers and followed a first-order behavior with very similar rate constants. These results, coupled with the fact that the compositions of copolymers were, within experimental error, the same as that of the corresponding monomer feed, were strong indications that the reactivity ratios in both these systems were close to unity. Such a conclusion is not surprising given the strong similarity between the monomer structures. However, it is important to emphasize that the use of the furan-containing monomer **3** did not lead to any detectable retarding reactions during the free radical copolymerizations; i.e., the heterocycle did not show any tendency to trap the active species, contrary to other furan-containing monomers.[19,25]

The homopolymer **6** and copolymers **7** displayed a marked tendency to cross-link when exposed to the atmosphere, as witnessed by their progressive insolubility. This feature can clearly be attributed to the lability of the hydrogen atom on the methylene group attached to the furan ring. Removal of these hydrogen atoms generates resonance-stabilized free radicals which can lead to their subsequent coupling. α-Hydrogen mobility in the form of proton, hydride ion, or atom, depending on the specific environment, is a common phenomenon with furan compounds because the dienic character of the heterocycle can stabilize all the three resulting intermediates,[19] namely, the carbanion, the carbenium ion, and the free radical. Given this pronounced reactivity, all furan-containing polymers were stored and chemically modified by the DA reaction under nitrogen.

The variation of the glass transition temperature from polystyrene to homopolymer **6** going through the two copolymers **7** and **8** is shown in Figure 6. The linear relationship with composition suggests that the copolymerizations were random processes, which confirms

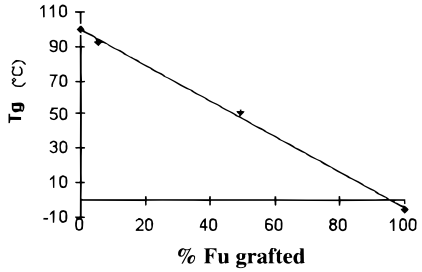

Figure 6. Variation of the glass transition temperature of (**1** + **3**) copolymers as a function of composition.

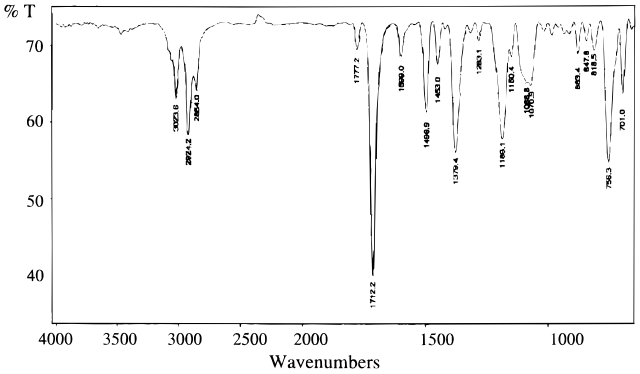

Figure 7. FTIR spectrum of **14**.

the "ideal" behavior ($r_1 \approx 1$ and $r_2 \approx 1$) found from their kinetic study. The progressive decrease in T_g as the concentration of the furan comonomer is increased can be explained by the fact that the length of the side group associated with the units from **3** introduces a hindrance to chain packing, as with long side-chain methacrylates, and thus a higher free volume fraction in the copolymer.

DA Coupling Applied to Polymers. It was decided to use only the copolymers obtained directly from monomers **3** + **1**, viz., **7b** and **8**, as substrates for the DA reactions in order to avoid the presence of trace amounts of chlorinated structures arising from the slightly incomplete etherification in **6a** and **7a**. The homopolymer **6b** was not tested in this context because of its excessive furan content, which might induce side reactions and complicate thereby the structural characterizations following both the DA and the RDA reactions.

In an initial series of experiments, the copolymers were treated with the monofunctional dienophile **12**. The sample of **7b** had $M_n = 47\,000$ and $M_w = 200\,000$; the sample of **8** had $M_n = 30\,000$ and $M_w = 54\,000$. Under the reaction conditions chosen, involving an excess of **12**, 65−70% of the pendant furan rings underwent the DA reaction, irrespective of the copolymer used. It seems likely that the equilibrium of the cycloaddition was attained for that conversion. The values were determined both by the elemental analysis (based mainly on the nitrogen content) and the ^{1}H-NMR spectra of the resulting polyadducts. The two methods gave results in very good agreement. Figures 7 and 8 show typical FTIR and ^{1}H-NMR spectra of the modified copolymer **14**. The corresponding spectra of the model adduct **9** were used as a reference for the interpretation of the polyadduct structures. All FTIR spectra of **14** and **15** showed the appearance (albeit with different intensity) of the adduct bands at 1777, 1712 cm^{-1} (C═O), 1379 and 1188 cm^{-1} (C−N), and 1088 cm^{-1} (C−O−C) and the strong decrease of the furanic peaks around 1600, 1500, 1015, 920, 880, and 820 cm^{-1}.

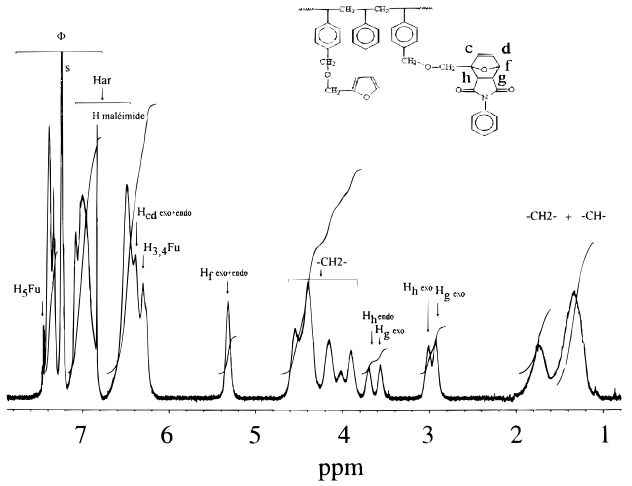

Figure 8. ^{1}H-NMR spectrum of **14** in $CDCl_3$.

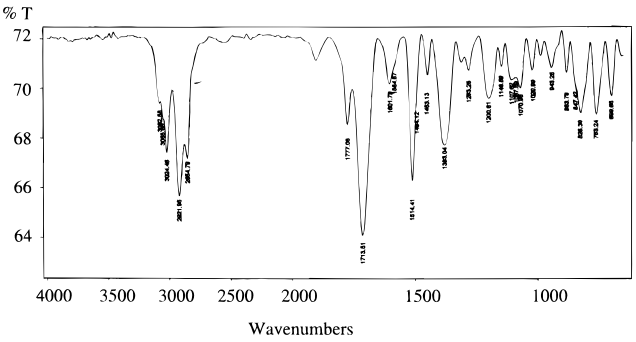

Figure 9. FTIR spectrum of **16**.

Figure 8 gives the assignments for the various resonances including those differentiating the exo- and endo-adducts. The polyadduct **14** had M_n = 49 000 and M_w = 220 000, whereas **15** had M_n = 29 000 and M_w = 57 000. These values are in excellent agreement with those of the corresponding starting copolymers.

In conclusion, the copolymers reacted efficiently with the monofunctional dienophile and this justified the next step, namely, the use of a bisdienophile of similar structure. The same copolymers were therefore treated with the bismaleimide **13**, but this time under stoichiometric conditions in order to optimize the intermolecular (cross-linking) reactions. With copolymer **7b**, the appearance of the gel occurred quite rapidly compared with the reaction involving **8**, as was indeed expected on the basis of the higher furan content of the former. However, both products **16** and **17** were isolated after 24 h. Blank reactions in the same conditions, but in the absence of **13,** were also carried out and showed that the copolymers were stable under the reaction conditions chosen, since no change in their structure could be detected by spectroscopic analysis.

Figure 9 shows a typical FTIR spectrum of the cross-linked material **16** in which the relevant bands for the formation of the bisadducts at 1777 and 1713 cm^{-1} (C═O), 1383 and 1200 cm^{-1} (C−N), and 1107 cm^{-1} (C−O−C) were detected and corroborated by comparison with the corresponding spectrum of model compound **10**. At the same time, the typical vibrational features arising from the furan heterocycle decreased strongly with respect to the spectrum of the initial copolymer **7b**. The yields of adducts formed could be estimated from the elemental analyses of the products (for **13**, C 78.57%, H 6.13%, O 12.85%, N 2.40%; for **14**, C 88.22%, H 7.35%, O 2.89%, N 0.7%), based on the assumption that all the nitrogen detected belonged to adduct moieties (i.e., there were no *free* pendant maleimide moieties arising from monoadduct formation). This gave a yield of 78 ± 10% for **16** and 112 ± 35% for **17**. The large experimental error on the latter value is due to the low nitrogen content (0.7%) arising from the correspondingly low furan content of starting copolymer **8**, coupled with the analytical error on this element (±0.2%). Of course with the initial copolymer **7a,** containing ten times more furan rings, the accuracy of the nitrogen content, and therefore the estimate of the extent of the DA reaction, was much better, although the presence of small amounts of bismaleimide structures with only one reacted group could not be excluded.

It can be concluded that copolymer **8**, bearing 5% of furan rings, gave a network involving most of the moieties available for the double DA reaction and therefore the cross-link density was close to the original furan content. Copolymer **7a**, with about 50% of pendant heterocycles, gave a network with a very high cross-link density resulting from the DA reaction of about 70% of these substituents.

RDA on Polyadducts and Gels. The study of the retro-Diels−Alder reaction of the polymeric adducts, conducted as specified in the Experimental Section, started with the simpler thermoplastic structures **14** and **15** prepared with the monofunctional dienophile. The spectroscopic analysis of the products recovered by precipitation into methanol confirmed that the reaction had indeed taken place. More specifically, **15** regenerated **8** quantitatively within 24 h, whereas **14** gave a polymer after 48 h whose ^{1}H-NMR spectrum was indistinguishible from that of **7a** (Figure 4) but whose FTIR spectrum showed a small additional carbonyl band apart from all the features characteristic of **7a**. The FTIR spectrum of the product isolated after 24 h of the RDA reaction carried out with **14** indicated that the reaction had taken place, but in a lower yield, as suggested by a carbonyl peak much less intense than that of the starting polyadduct but stronger than that exhibited by the polymer isolated after 48 h. Figure 10 shows these features as compared with those of Figure 7. These results strongly suggest that even with a high content of adducts, complete conversion into the original copolymers by RDA is kinetically feasible. Indeed, the very small carbonyl peak after 48 h indicates either a minute content of residual adducts (not detected by ^{1}H NMR) or the occurrence of a minor side reaction leading to carbonyl functions. The molecular weight of the recovered polymer was only slightly higher than that of the starting material: thus, with a sample of **8** with M_n = 30 500 and M_w = 58 500 we prepared the corresponding polyadduct **15** which gave M_n = 37 000 and M_w = 78 000 and after the RDA reaction, the recovered product had M_n = 33 500 and M_w = 86 000. The spectroscopic analysis of the methanol-soluble product of these RDA reactions confirmed that it was the expected model adduct **9**, arising here from the DA reaction between the liberated maleimide **12** and the excess of **11** present in the medium.

These results encouraged us to move onto the application of the RDA reaction to the gelled products **16** and **17**. The visual test of the occurrence of this reaction was the progressive dissolution of the starting materials. With **17**, only 3 h were necessary to solubilize the whole sample, but the system was left for a total of 24

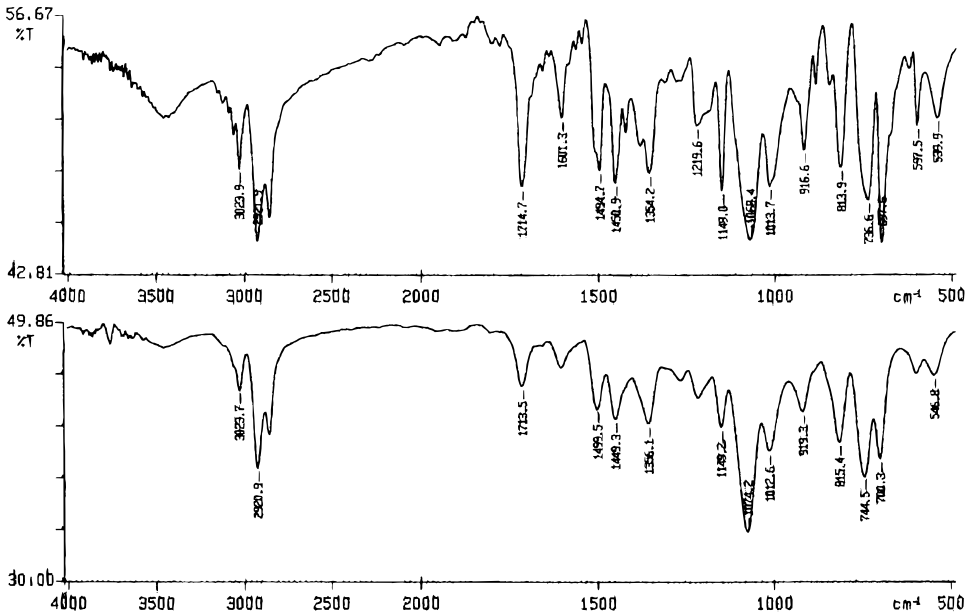

Figure 10. FTIR spectra of polymer **14** submitted to the RDA reaction. Top, after 24 h; bottom, after 48 h.

h. The precipitation and characterization of the ensuing polymer revealed that **8** had been totally regenerated, i.e., that the RDA reaction had reached completion. The molecular weights of the polymer thus recovered were $M_n = 40\ 500$ and $M_w = 159\ 000$, viz., somewhat higher than those of the starting copolymer **8**. With **16**, incomplete dissolution was observed after 48 h. The FTIR of the polymeric reaction product indicated a very strong decrease of the C=O band, and the ^{1}H-NMR spectrum on the soluble part was identical to that of copolymer **7b** (Figure 4). In both instances, the methanol-soluble residue was again isolated and analyzed. Its spectroscopic features coincided with those of model compound **10**, thus confirming the occurrence of the RDA reaction followed by the DA reaction of the liberated bismaleimide **13** with the excess of **11**.

All the above evidence leaves no doubt about the reversibility of the different DA reactions applied to the furan-containing copolymers prepared in this work. As to its quantitative aspect, whereas macromolecular structures bearing modest amounts of pendant heterocycles showed a total reversibility, with 50% of such moieties, the RDA reactions did not regenerate entirely the copolymers in their original form. Whether this is to be attributed to kinetic reasons, viz., incomplete reaction, or to the occurrence of minor side reactions which modified the adducts and inhibited their aptitude to undego the RDA pathway remains to be established. These side reactions could arise from free-radical interactions involving the unsaturation present in the maleimide moieties (such as in a monosubstituted pendant group or in the adduct structure) and/or in the adduct structures or from the aromatization of the adducts. The former mechanism seems more likely in view of the relatively modest temperatures used in our RDA systems compared with those typically required to transform the adducts into aromatic moieties.

The use of copolymer **7b**, bearing 50% of furan moieties, has little quantitative relevance to the main aim of this investigation which was to show that reversible cross-linking through the DA-RDA reactions is possible with furan-containing polymers. In fact, the DA reaction in this context can lead to a network already with less than 2% of pendant furan rings in a copolymer.[9] The main reason for testing such a furan-rich copolymer was to monitor adequately the various reactions taking place during the DA-RDA cycles. Copolymer **8** gave a very satisfactory behavior in terms of both reactivity and reversibility with 5% of furan rings. This content is realistic for a material capable of cross-linking, although it should be possible to halve it, as with elastomers to be vulcanized, e.g., isobutene−isoprene copolymers.

The occurrence of irreversible structural changes in the gels was very apparent when these materials were analyzed by TGA under nitrogen. Both **16** and **17** showed a remarkable stability in terms of weight loss since the samples kept their mass up to ca. 350 °C. In these conditions it seems reasonable to assume that the RDA reaction occurred only partially, because the samples were heated rather rapidly (20 °C min^{-1}) leaving too little time for the poorly volatile bismaleimide to vaporize. As a consequence, aromatization and/or free-radical reactions involving the unsaturations gave rise at high temperature to a product with good thermal stability. This behavior was therefore radically different from that observed when the same gels were submitted to the milder and more conducive conditions chosen to favor the RDA reaction.

Conclusion

The possibility of modifying, in high yields, polymers and copolymers bearing pendant furan rings, by means of the Diels−Alder reaction has been verified for both mono and bisdienophiles. The retro-Diels−Alder reaction has also been carried out successfully by the use of an excess of a furan trap which displaced the equilibrium involving the polymeric adducts. The reversibility of these operations was very satisfactory when modest adduct densities were involved, whether with linear structures or with cross-linked materials. When the percentage of furan moieties was high, some cycloadducts seemed to lose their ability to revert to the original structures, probably because of side reactions, although a purely kinetic problem cannot be excluded. In any event, the idea of applying these concepts to elastomeric

networks (formed through double intermolecular DA reactions) which could be recycled by their return to thermoplastic properties through the RDA pathway was validated by this investigation. Indeed, in a typical vulcanized rubber, the cross-link density is only between 2 and 3%, i.e., even lower than that of the double-DA-modified 5% furanic copolymer networks, which gave total RDA-based reversibility.

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